narrowing condition can be satisfied. For a rodlike chain molecule like amino acids in a viscous medium such as aqueous solution this condition will not in general be satisfied very well, and then all three modes $\nu_1$, $\nu_2$, and $\nu_3$ may remain coupled to one another. This in turn will give the solution $R(t)$ as a combination of three exponential terms, which explains why the combination of only two exponential terms failed to explain the relaxation of methyl protons in this case. Only way to get out of trouble in this situation is to treat the methyl group as an $A_3X$ system, including $^{13}C$ besides three protons, and obtain the data for as many observable modes as possible. Application of this technique to a few examples is under investigation in our laboratory.

## Concluding Remarks

It was found that at room temperature or below the spin-lattice relaxation of $^{19}F$ in benzotrifluoride could be well described by a two-parameter equation given explicitly in Eq. (16) which was derived under the assumption that modulation of interactions in the spin system, both dipole-dipole and spin-rotation, is caused predominantly by internal rotational motions in the molecule, and the separation of contribution due to dipolar interactions from that due to spin-rotation interaction was successfully achieved by least-square fitting of observed data to this equation. As expected, the spin-rotational contribution was found to overwhelm that of dipolar origin over the temperature range of 248-268 K and becomes more dominating at higher temperature.

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# Transition Rates in a Bistable System Driven by Singular External Forces

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A noise-induced transition is presented for a bistable system subjected to a multiplicative random force, which is singular at the unstable state. The stationary probability distribution is obtained from the Fokker-Planck equation and the effects of the singularity is analyzed. On the basis of noise-induced phase transition with Gaussian white noise, the relaxation time and the transition rate of the system are evaluated up to the first order correction of D. In the parameter region $\nu<1$, the transition rates decrease as the exponent $\nu$ goes to 1 and as the coefficient of the linear term of the kinetic equation increases.

## Introduction

In recent years there have been increasing interests in the investigation of the dynamic properties in the fluctuating nonlinear system. In particular, a number of papers have been devoted to the study of relaxation times (or mean first-passage times) and transition rates in bistable systems driven by random forces[1-3]. Depending on the properties of the

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random force, various methods have been applied to this problem. In the case of Gaussian random force with white noise (short correlation time) the properties of the system are investigated from the Fokker-Planck equation (FPE) which describes a fluctuating nonlinear system[4,5]. On the other hand, the systems with colored noise are studied by using the stochastic trajectory analysis[3]. However, the investigation of the dynamic properties in the bistable system driven by multiplicative random forces is far more complicated. We are going to evaluate the relaxation times and transition rates in multiplicative fluctuating bistable systems described by the following Langevin equation[4,6].

$$\frac{d}{dt}x+h(x)+g(x)\Gamma(t) \tag{1}$$

where $h(x)$ is the deterministic term of a kinetic equation and a cubic polynomial and $\Gamma(t)$ is a random force. The function $g(x)$ describes the coupling between the deterministic term and the random force and reflects the fact that this coupling may depend on the concentration of the system.

In the bistable system there are three steady states. The one of the stationary states is unstable and the rests are stable. In the absence of the noise, transitions between two stable steady states cannot occur since the system evolves according to the deterministic equation. If external force is applied to such a bistable system, the dynamical system may evolve to either of two asymptotic stable states and cause transition between the coexisting steady states. If the system stays mainly near the deterministic steady states, a transition rate between these steady states can be evaluated by applying a noise induced rate process. This dynamic bebavior is shown in many systems, physical[5], chemical[1,7], and biochemical system[8-10].

Let us consider the following mechanism of chemical reaction[8]

$$\begin{aligned} &A \xrightarrow{k_1} X, \\ &B+X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 3X+C, \\ &D+X \xrightarrow{k_3} E, \end{aligned} \tag{2}$$

with the reactants and products A, B, C, D, and E assumed to have constant concentration and $k_i$'s being rate constants of elementary reactions. Then, the kinetic equation is written as

$$\frac{d}{dt}X=-Ck_{-2}X^3+(Bk_2-Dk_3)X+Ak_1 \tag{3}$$

If the system is completely homogeneous, after a suitable scaling we can rewrite a kinetic equation as

$$\frac{d}{dt}X=-X^3+\rho X+\eta, \tag{4}$$

where the scaling constants are

$$t=t/Ck_{-2},\ \rho=(Bk_2-Dk_3)/Ck_{-2},\ \text{and}\ \eta=Ak_1/Ck_{-2}.$$

According to the stability analysis there are three steady states[13] under the following conditions $\rho>0$ and $0<\eta<2(\rho/3)^{3/2}$. Near the steady state far from equilibrium the concentration $X(t)$ may be written in terms of $X_i(t)=X_i^{\circ}+x_i(t)$. By using the deviation from the steady state the kinetic equation becomes

$$\frac{d}{dt}x-h(x)=\mu x-x^3, \tag{5}$$

where $\mu$ is assumed to be positive and defined as $\mu=\rho-3X^{\circ 2}>0$.

If the nonlinear homogeneous system is subjected to external multiplicative noise, the Langevin equation is expressed as

$$\frac{d}{dt}x=\mu x-x^3+|x|^{\nu}\ \Gamma(t) \tag{6}$$

where $\nu$ need not to be restricted to an integer. Although the multiplicative fluctuating nonlinear system is dealt with in numerous papers, the FPE derived from the above Langevin equation has not been sufficiently investigated. In particular, only the equation with $\nu=1$ and $\nu=0$ has been mainly investigated. Recently, G. Hu and K. He[4] have investigated the dynamic properties by using the FPE for the system with $\mu=1$. A noise-induced phase transition is mainly due to the multiplicative noise $|x|^{\nu}$ which determines the property of the system. However, it is much more complicated to investigate the dynamic properties for the chemical system with singularity. The chacteristics of the system are such that the unstable singular point of the deterministic is located identically to the point of the noise-induced system. The characteristics of the system are such that at an unstable state the behavior of the system is dramatically changed.

In this paper the dynamic behaviors of the system is investigated in all possible $\nu$ values. In Sec. II., the stability of the system will be analyzed and the stationary distribution will be calculated from the FPE. In Sec. III., using a suitable transformation of the variable $x$, the Langevin equation with multiplicative random force will be transformed into the equation with additive random force. In the parameter region $\nu<1$ we obtain up to the first order of diffusion coefficient the result for the relaxation time and the transition rate between both stable states. The results and discussion are given in Sec. IV.

## II. Stationary Probability Distributions

The deterministic system has one unstable point $x=0$ and two stable points $x=\pm\mu^{1/2}$. Then, the system has the instrinsic feature that the unstable point of the deterministic system is located identically to the singular point of the random force. The random force is assumed to satisfy the Gaussian condition for the correlation time $\tau(=t-t')\to 0$

$$\langle\Gamma(t)\rangle=0,\ \langle\Gamma(t)\Gamma(t')\rangle=2D\delta(t-t'), \tag{7}$$

where $D$ is the diffusion coefficient and $\delta(t-t')$ is the Dirac delta function. The FPE corresponding to Eq. (6) is derived as

$$\frac{\partial}{\partial t}P(x,\ t)=-\frac{\partial}{\partial x}\left\{\mu x-x^3-D\frac{\partial}{\partial x}|x|^{\nu}\right\}P(x,\ t). \tag{8}$$

The stationary solution of the FPE gives the stationary probaility distribution as

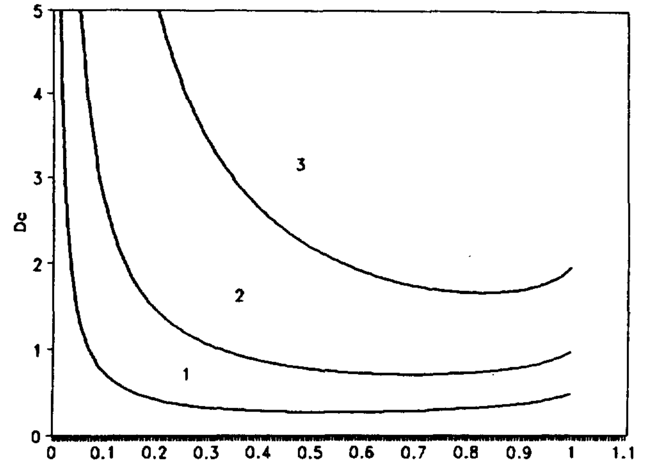

**Figure 1.** The phase diagram in v-$D$ plane. The curves are shown the critical values of $D$ versus v. The porfiles 1, 2, and 3 correspond to $\mu=0.5$, $\mu=1$, and $\mu=2$, respectively.

$$P(x,\ 0)=A|x|^{-\nu}\ \exp\left\{\frac{1}{D}\left[\frac{\mu}{2-2\nu}|x|^{2-2\nu}-\frac{1}{4-2\nu}|x|^{4-2\nu}\right]\right\}. \tag{9}$$

The maxima of the probability (corresponding to potential well) appear at the solution of the equation

$$x^{4-2\nu}-\mu x^{2-2\nu}+\nu D=0 \tag{10}$$

Using the Newton's method of successive approximation[13] we obtained the two stable points

$$x_{1,2}\cong\pm\mu^{1/2}\mp\frac{\nu D}{2}\mu^{-(2-\nu)}. \tag{11}$$

In the case for which $\nu>1$, and $\nu<0$, the probability at the unstable point $x=0$ approaches to zero. On the other hand, in the region for which $0<\nu<1$ when $x\rightarrow 0$, the probability distribution is divergent to positive infinite and near the unstable point there are different two minima of the probability distribution besides two maxima.

$$x_{3,4}=\pm\left[\frac{\nu D}{\mu}\right]^{1/[2(1-\nu)]} \tag{12}$$

This minima disappear at the critical condition[14,15]. Increasing $D$, the minimum and maximum get closer to the critical value $x_c$

$$D_c=\frac{\mu^{2-\nu}}{\nu}\left\{\left[\frac{(1-\nu)}{2-\nu}\right]^{1-\nu}-\left[\frac{(1-\nu)}{2-\nu}\right]^{2-\nu}\right\} \tag{13}$$

The critical value $D_c$ depends not only on the parameter v but also on μ in potential. The phase diagram is shown in Figure 1 and we take $\mu=0.5$, $\mu=1$, and $\mu=2$, respectively. With increasing μ value, $D_c$ decreases. The critical $D_c$ decreases as v approaches to 1. If $D$ is larger than $D_c$, the maximimum and the minimum point of the probability distribution disappear and the maximum peak appear at the origin which is an unstable point of the deterministic term.

The probability distribution given in Eq. (9) have the symmetry property with respect to $x$ and the behavior of the probability display very interesting characteristics near the deterministic unstable point. With respect to the parameter v region, the singular Langevin force $|x|^{\nu}\,\Gamma(t)$ plays an important role in noise induced phase transition. As $x$ approaches the unstable point ($x\rightarrow 0$), $|x|^{-\nu}$ term due to the random force goes to positive infinity when $\nu>0$ and it goes to zero

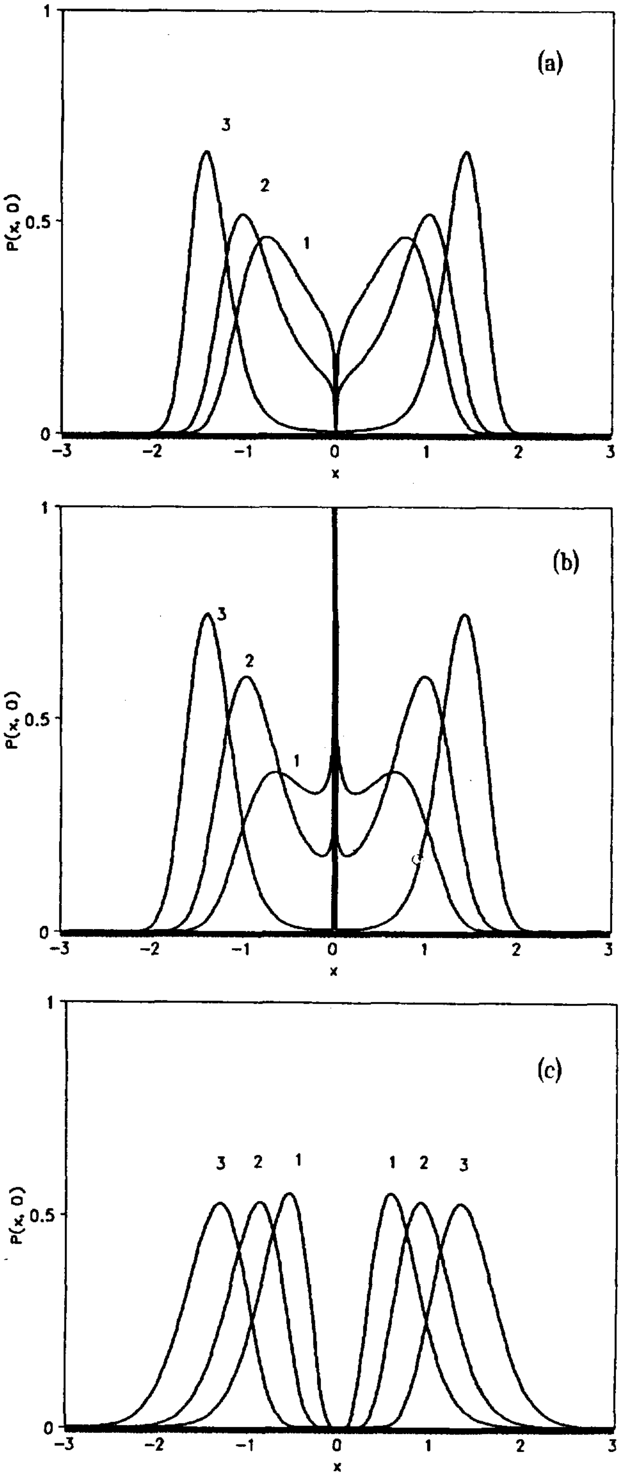

**Figure 2.** When $D=0.2$ the stationary probability distributions in the three regions. The profiles 1, 2, and 3 correspond to $\mu=0.5$, $\mu=1$, and $\mu=2$, respectively. (a) In the region v± 0, the distributions were taken at $\nu=-0.2$. (b) In the region $0<\nu<1$, the distributions were taken at $\nu=0.5$. (c) In the region $\nu>1$, the distributions were taken at $\nu=1.2$.

when $\nu<0$, while the exponential function due to drift term approaches zero in the regoin $\nu>1$. and in the case $\nu<1$ it has a finite value. Thus, we can consider that the parameter region divided into three part as shown in Figure 2. (i) In the case $\nu<0$, the probability at the origin disappears because the random force is infinitely strong near the unstable point ($x\rightarrow 0$). As shown in Figure 2(a), the distribution has a narrow hole at the unstable point and the hole becomes narrower as $\nu$ increases and $\mu$ decreases. (ii) In the region $0<\nu<1$, since as $x\rightarrow 0$ the random force decreases slowly, the system is controlled by the random force and as $x\rightarrow 0$ the probability diverges. In Figure 2(b) when $\nu=0.2$, we take $\mu=0.5$ (curve 1), $\mu=1$ (curve 2), and $\mu=2$ (curve 3). The minimal distribution goes to zero as $\nu$ increases and $\mu$ increases. (iii) In the region $\nu>1$, since the random force decreases fast, the probability is governed by the drift force and approaches 0 as $x\rightarrow 0$. In Figure 2(c), as $\nu=1.2$, we fix $\mu=0.5$, $\mu=1$, and $\mu=2$. As $\nu$ increases the central hole is enlarged and two peaks become closer and closer. Increasing $\mu$ the two peaks become further apart. Thus, the noise-inducing phase transition phenomena may be observed only in the case for which $\nu<1$. In the following section, we will transform the FPE with multiplicative random noise to the FPE with additive noise and then the relaxation time and transition rate is evaluated.

## III. Relaxation Time and Transition Rate

Let us consider the system for which the kinetic equation is described as the multiplicative Langevin Eq. (6). It is certain that in the white noise limit ($D\rightarrow 0$) the dynamic behaviors of the system are closely related to the stationary solution. The time-dependent solution may have essentially different characters because of the singularity of multiplicative random force. To facilitate the treatment of the singularity we will introduce a new variable $y$ defined by[4]

$$y=\begin{cases} |x|^{\varepsilon}, \text{ for } x>0. \\ -|x|^{\varepsilon}, \text{ for } x<0. \end{cases} \tag{14}$$

where $\varepsilon=1-\nu$. In the case that $\nu>1$, the reduced variable $y\rightarrow\infty$ as the concentration $x$ goes to zero. In the parameter region $\nu<1$, the reduced variable $y\rightarrow 0$ as the concentration $x$ goes to zero. The Langevin Eq. (6) is reduced to

$$\frac{d}{dt}y=f(y)+\varepsilon\ \Gamma(t), \tag{15}$$

where for $y>0$

$$f(y)=\varepsilon\{y-y^{(2+\varepsilon)/\varepsilon}\} \tag{16}$$

and the function is symmetric against origin. It is obvious that the function $f(y)$ is smooth and the concentration $y(t)$ never diverges to infinite in a finite time. The Fokker-Planck equation for the probability distribution $P(y, t)$ corresponding to the Langevin Eq. (16) has the following form:

$$\frac{\partial}{\partial t}P(y,\ t)=L(y)P(y,\ t)=-\frac{\partial}{\partial y}S(y,\ t); \tag{17}$$

where the probability current $S(y, t)$ is given as

$$S(y,\ t)=\left\{f(y)-d\frac{\partial}{\partial y}\right\}P(y,\ t), \tag{18}$$

and $L(y)$ is the Fokker-Planck operator which is described as

$$L(y)=-\frac{\partial}{\partial y}\left\{f(y)-d\frac{\partial}{\partial y}\right\}, \tag{19}$$

and the reduced diffusion coefficient $d$ is

$$d=\varepsilon^2\ D \tag{20}$$

In the stationary state the probability current in the FPE must be constant and then the stationary probability distribution is described as

$$P_{st}(y)=C\ \exp\{-V(y)/d\}, \tag{21}$$

where $C$ is normalization constant and the potential function is introduced as follows

$$V(y)=-\int^{y} f(y)\ dy. \tag{22}$$

In the bistable system, the deterministic Eq. has three real roots. Two of these, $y_1$ and $y_2$, are stable and correspond to minima of the potenial. The third root, $y_u$, is unstable and therefore corresponds to a maximum of the potential. It is assumed that the system initially lies in the vicinity of one of the minima of the potential ($y_1$ or $y_2$). In gereral, the final state is either the maximum of the potential or the other minimum. In latter case the MFPT is twice the former case. Introducing the potential of the system the Fokker-Planck operator may be written as

$$E(y)=\frac{\partial}{\partial y}\left\{d\ \exp\{-V(y)/d\}\ \frac{\partial}{\partial y}\left[\exp\{V(y)/d\}\right]\right\} \tag{23}$$

If the stochastic variable cannot reach values smaller than $y_{min}$, the current must be zero at the stationary state.

In order to obtain the nonstationary solution of the FPE we separate the probability distribution as follows

$$P(y,\ t)=\varphi(y)\ \exp(-\lambda t), \tag{24}$$

where $\varphi(y)$ and $\lambda$ are the eigenfunctions and eigenvalues of the Fokker-Planck operator with appropriate boundary conditions. The operator is not Hermitian, but can be transformed into Hermitian form[5] with the aid of the potential function $\exp\{V(y)/2d\}$. If $\psi(y)$ are the eigenfunctions of the Fokker-Planck operator with the eigenvalues $\lambda$, the eigenfunctions of the transformed operator with the same eigenvalues $\lambda$ are expressed as

$$\psi_n(y)=\exp\{V(y)/2d\}\ \varphi_n(y) \tag{25}$$

In order to calculate the transition rate we have to determine the lowest eigenvalue for a bistable potential and a metastable potential. The lowest nonvanishing eigenvalue is related to the transition rate form one well to another well of potential. It is assumed that at $y=\pm B$ the potential has absorbing wall (small potential barrier). This assumption is fairly reasonable because the potential function diverges as $y$ goes to infinite. Because the probability current must be zero (reflecting wall) at $y=B$, we can obtain the eigenfunction of the Fokker-Planck operator by integrating the following differential equation

$$d\frac{\partial}{\partial y}\left\{\exp\{-V(y)/d\}\frac{\partial}{\partial y}\left[\exp\{V(y)/d\}\right]\right\}\varphi(y)=-\lambda\varphi(y). \tag{26}$$

By integrating the above equation from $x$ to $B$, the eigenfunction is given as

$$\varphi_n(y)=\exp\{\Delta V(B,\ y)/d\}\ \varphi_n(B)$$

$$\left\{1-\frac{\lambda_0}{d}\exp\{-V(B)/d\}\int_0^y dy\ \exp\{V(y)/d\}\int_0^y \varphi(z)\ dz\right\}, \qquad (27)$$

with the boundary condition

$$\varphi_0(B)=0, \qquad (28)$$

where the potential barrier $\Delta V$ is written as

$$\Delta V(y_1,\ y_2)=V(y_1)-V(y_2). \qquad (29)$$

For large potential barrer height[5] since the eigenvalue $\lambda_0/d$ will be very small, the lowest eigenfunction is

$$\varphi_0(y)=\exp\{\Delta V(B,\ y)/d\}\ \varphi_0(0) \qquad (30)$$

By inserting Eq. (30) into the integral of Eq (27) we obtain the first order approximation for the eigenfunction

$$\varphi_0(y)=\exp\{\Delta V(0,\ y)/d\}\ \varphi_0(0)$$

$$\left\{1-\frac{\lambda_0}{d}\int_0^y dy\ \exp\{V(y)/d\}\int_0^y \exp\{-V(z)/d\}\ dz\right\}, \qquad (31)$$

According to the boundary condition the eigenvalue up to the first order approximation is given by

$$\lambda_0=d\left[\int_0^B dy\ \exp\{V(y)/d\}\int_0^y \exp\{-V(z)/d\}\ dz\right]^{-1} \qquad (32)$$

For small diffusion limit the double integral can be evaluated analytically. Because the integral has a very sharp maximum at $y=y_1$ and $z=y_u$ we expand the potential function around the maximum point up to the fourth order. This eigenvalue $\lambda$ is regarded as the relaxation time from one stable state to an unstable state.

The relationship between relaxation time and the transition rate from one well to the other of the bistable potential is[3,5]

$$T\simeq 1/2\lambda \qquad (33)$$

In order to obtain the eigenvalue we must calculate the integrals in Eq. (32). By using an expansion in the potential up to fourth order term[3,5] and then evaluating the integrals in Eq. (32) we obtain the relaxation time as follows

$$T=T_0\{1+AD+O(D^2)\}, \qquad (34)$$

where

$$A=\frac{3}{4}\left\{\frac{\gamma_u}{\alpha_u{}^2}-\frac{\gamma_1}{\alpha_1{}^2}\right\}+\frac{15}{16}\left\{\frac{\beta_u{}^2}{|\alpha_u|^3}+\frac{\beta_1{}^2}{\alpha_1{}^3}\right\},$$

and

$$\beta_{1,u}=\frac{V'''(y_1,\ y_u)}{6}\ \text{and}\ \gamma_{1,u}=\frac{V^{(IV)}(y_1,\ y_u)}{24} \qquad (35)$$

The relaxation time $T_0$ is the well-known Kramers' relaxation time given by

$$T_0=\frac{\pi}{2(\alpha_1|\alpha_u|)^{1/2}}\exp\{\Delta V(y_u,\ y_1)/d\} \qquad (36)$$

where

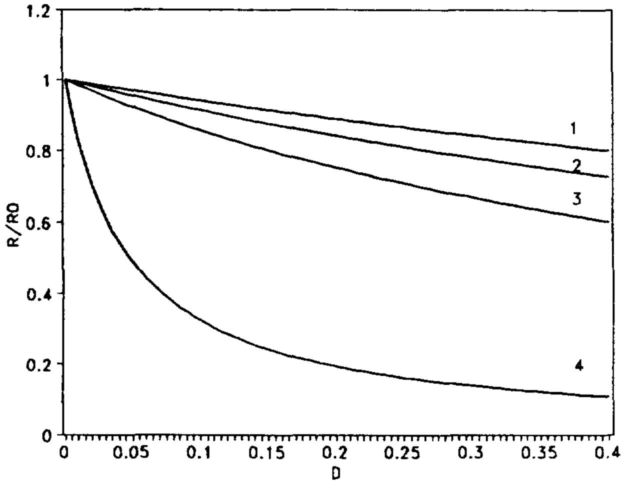

**Figure 3.** The ratio of $R/R_0$ for the bistable system with $\mu=1$. The curves 1, 2, 3, and 4 correspond to $\nu=-0.2$, $\nu=0.2$, $\nu=0.5$, and $\nu=0.9$, respectively.

$$\alpha_{1,u}=\frac{V''(y_1,\ y_u)}{2} \qquad (37)$$

For a symmetric potential $\beta_u=0$ and $\gamma_1=0$. The transition rate $R$ from one well to the other of the bistable potential is equal to the inverse of the relaxation time

$$R\simeq 1/T \qquad (38)$$

Using the results given in Eqs. (34) and (38), the relaxation times and the transition rates are evaluated in the following section.

## Results and Discussion

We have obtained the transition rate in the bistable chemical system with the multiplicative random force, $g(x)=|x|^\nu$. The result of this paper is embodied in Eqs. (34) and (38). These are expressions for the transition rate when the correlation time of the random force is short. The multiplicative noise-induced transition from one well to the other is applied to chemical reaction with nonlinearity. The result recovers the correct white-noise limiting behavior, which is identical to that of a bistable system driven by Gaussian white noise. The correction up to first order $O(D)$ need derivatives of the potential functionto fourth order. The transition rate from one minimum potental to another minimum potental can be evaluated on the basis of the Fokker-Planck equation with Gaussian additive noise. The transition rate is easily calculated by the relaxation givn in Eq. (37).

$$R=R_0\left[1+D\left(\frac{(3-\nu)\ (3-2\nu)}{12}\right)\mu^{\nu-2}+O(D^2)\right]^{-1} \qquad (39)$$

where $R_0$ is the transition rate evaluated by G. Hu and K. He[4].

$$R_0=\frac{\mu}{\pi}\{2(1-\nu)\}^{1/2}\ \exp\left\{-\frac{\mu^{2-\nu}}{(4-2\nu)(1-\nu)D}\right\} \qquad (40)$$

The results for the ratio $R$ to $R_0$ are shown in Figure 3 and Figure 4. In Figure 3 we have taken the coefficient $\mu$ in the potential to be unity and $\nu=-0.2$, $\nu=0.2$, $\nu=0.5$,

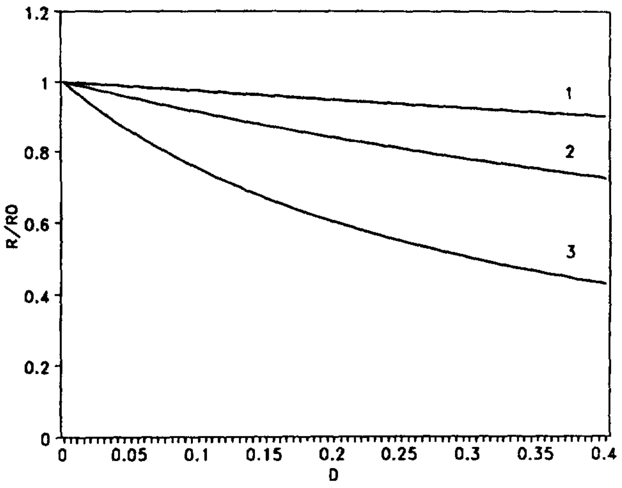

**Figure 4.** The ratio of $R/R_0$ for the bistable system with $\nu=0.2$. The curves 1, 2, and 3 correspond to $\mu=0.5$, $\mu=1$, and $\mu=2$, respectively.

and $\nu=0.9$, respectively. In Figure 4 we have taken $\mu$ to be 0.5, 1, and 2, respectively, when $\nu=0.2$. As $D$ increases the ratio in large $\mu$ value decreases faster than the ratio in small $\mu$ does. As shown in Figure 3, it is obvious that in the region $\nu<1$ the transition rates decrease with increasing $D$. As the exponent $\nu$ increases, the transition rates decrease and relaxation times increase. In the limit $\nu \rightarrow 1$, the transition rate approaches zero.

In the result, in the region for which $\nu<1$ the transition rates decrease as $\nu$ increases and $\nu$ decreases shown in Figure 3 and 4. However, in the case that $\nu>1$, it is obvious that in Eq. (17) never probability can be reach $y \rightarrow \infty$ in any finite time. It means that the system cannot be reach the unstable state since the concentration $x \rightarrow 0$ (unstable point) corresponds to $y \rightarrow \infty$. When $\nu>1$ the random force is so weak that the system is entirely controlled by the deterministic term in the vicinity of the unstable state. The transition between the two deterministic stable states cannot occur and the initial distribution is continuously retained.

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# Orbital Interactions in $BeC_2H_2$ and $LiC_2H_2$ Complexes

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*Ab initio* calculations are carried out at the 6-311G** level for the $C_{2v}$ interactions of Be and Li atoms with acetylene molecule. The main contribution to the deep minima on the $^3B_2$ $BeC_2H_2$ and $^2B_2$ $LiC_2H_2$ potential energy curves is the $b_2$ ($2p(3b_2)-|\pi_g^*(4b_2)$) interaction, the $a_1$ ($2s(6a_1)-|\pi_u(5a_1)$) interaction playing a relatively minor role. The exo deflection of the C-H bonds is basically favored, as in the $b_2$ interaction, due to steric crowding between the metal and $H$ atoms, but the strong in-phase orbital interaction, or mixing, of the $a_1$ symmetry hydrogen orbital with the $5a'_1$, $6a'_1$ and $7a'_1$ orbitals can cause a small endo deflection in the repulsive complexes. The Be complex is more stable than the Li complex due to the double occupancy of the $2s$ orbital in Be. The stability and structure of the $MC_2H_2$ complexes are in general determined by the occupancy of the singly occupied frontier orbitals.

## Introduction

The interactions of metal atoms with molecules have been the subject of many experimental and theoretical studies.[1] The main purpose of the research in this field is a fundamental understanding of catalysis. It has been suggested that